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Structural Geometry, Electronic and Quantum Chemical Investigations of Symmetrical Acetylenic Analogues of Tetrathiafulvalenes (TTF)



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ABSTRACT

In this study, structural geometries, Natural Bond Orbital (NBO) and Non-Linear Optical (NLO) analysis was performed of symmetrical acetylenic analogues of TTF **1-4** in the ground state were calculated by using Density Functional Theory (DFT-B3LYP/6-31G(d,p)) method. The total electron density and electrostatic potential of the title compounds are determined by natural bond orbital analysis. Various reactivity and selectivity descriptors such as chemical hardness, chemical potential, softness, electrophilicity, nucleophilicity and Fukui functions were calculated by same method cited above.



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1. INTRODUCTION

Recently, the Tetrathiafulvalenes (TTFs) have become an interesting theme of organic synthesis. This is due to the high electrical conductivity and superconductor properties of these highly sophisticated compounds ^[1]. It was also reported that the tetrathiafulvalenes have a good π -donor ability ^[2].

TTF as the most important electron donor has received much attention and a vast number of new TTF donors has been synthesized and investigated, such as tetrathiafulvalenylallene ^[3], TTF oligomers ^[4,5], and π -extended TTF derivatives ^[6]. Up until now TTF derivatives have found their applications in various fields including molecular logic gates ^[7], molecular switches ^[8,9], semiconductors ^[10,11], organogelators ^[12], liquid crystals ^[13,14], dyes absorbing over the whole visible spectrum ^[15], sensors for proton, cations or anions ^[16-18], and ligands ^[19-22].

TTF is well known for its electron donor ability, which has been exploited to construct a breadth of molecular devices ^[23], including photo and electroactive donor-acceptor dyads and triads ^[24], organic field-effect transistors ^[25], cation sensors and bistable molecular shuttles and catenanes ^[26-29]. Its π -extended analogues in which the 1,3 dithiole rings are covalently connected to a π -conjugated core have mainly been exploited as electron donor fragments in covalently linked donor-acceptor conjugates ^[24]. In contrast, while the supramolecular chemistry of TTF is nowadays a well-trodden path ^[30,31], that of its π -extended analogues had remained virtually unexplored.

Density functional Theory (DFT) is a Quantum-Mechanical (QM) method used in chemistry and physics to calculate the electronic structure of atoms, molecules and solids. It has been very popular in computational solid-state physics since the 1970s. The real forte of DFT is its favourable price/performance ratio compared with electron-correlated wave function-based methods such as Møller-Plesset perturbation theory or coupled cluster. Thus, larger (and often more relevant) molecular systems can be studied with sufficient accuracy, thereby expanding the predictive power inherent in electronic structure theory ^[32].

In this perspective, we have study a various characters of symmetrical acetylenic analogues of TTF **1-4** described in literature ^[33]. The total energy, HOMO and LUMO energies, the $\Delta E_{\text{LUMO}} - \text{HOMO}$ energy gap, and global reactivity descriptors like global hardness (η), global

softness (s), chemical potential (μ), and electrophilicity index (ω) calculations were computed by using TD-DFT/B3LYP/6-31G(d,p) method.

2. MATERIALS AND METHODS

The optimized geometries and total energies of symmetrical acetylenic analogues of TTF **1-4** were computed employing the DFT^[34] using Gaussian 09 program package^[35] and Becke's three parameter with Lee-Yang-Parr hybrid correlation functional (B3LYP)^[36-38]. The basis set 6-31G(d,p) augmented by 'd' polarization functions on heavy atoms and 'p' polarization functions on hydrogen atoms were used^[39,40].

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

The optimized bond lengths, bond angles and dihedral angles of symmetrical acetylenic analogues of TTF **1-4** obtained for the studied compounds using the B3LYP method with 6-31G(d,p) basis set are given in Tables 1-4; while the atom numbering of the optimized structure are given in Fig 1. The studied compounds possesses C₁ point group.

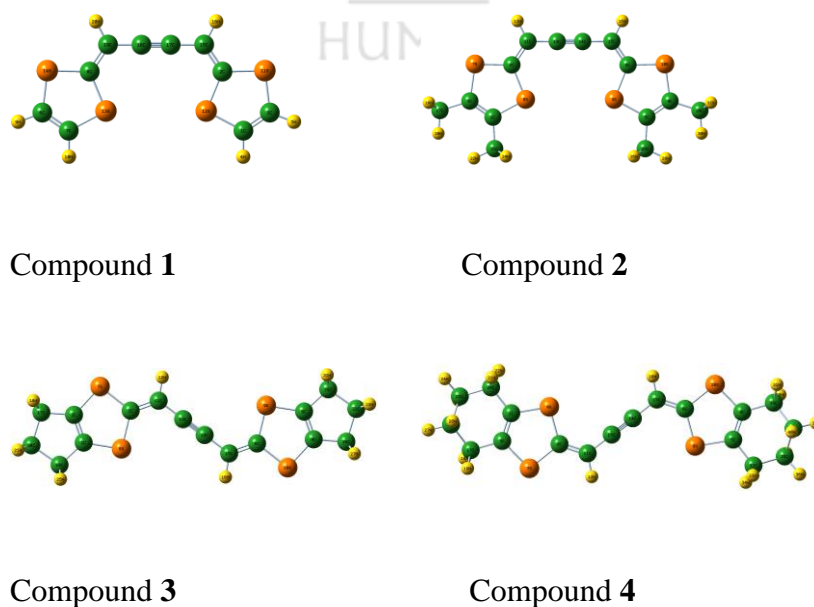


Figure 1. Optimized molecular structure of symmetrical acetylenic analogues of TTF 1-

Table 1.Optimized geometric parameters of compound 1

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,3)	1.338	A(3,1,4)	124.698	D(12,1,3,5)	180.000
R(1,4)	1.083	A(3,1,12)	118.024	D(15,2,11,3)	179.999
R(1,12)	1.760	A(4,1,12)	117.277	D(12,2,15,16)	180.000
R(2,12)	1.777	A(11,2,12)	113.784	D(9,6,7,13)	180.000
R(2,15)	1.361	A(12,2,15)	123.314	D(9,6,14,8)	180.000
R(6,7)	1.338	A(7,6,9)	125.113	D(19,8,14,6)	179.999
R(6,9)	1.082	A(7,6,14)	117.525	D(4,1,3,11)	180.000
R(6,14)	1.759	A(9,6,14)	117.361	D(4,1,12,2)	180.000
R(8,14)	1.778	A(13,8,14)	113.784	D(15,2,12,1)	179.999
R(8,19)	1.361	A(14,8,19)	122.900	D(11,2,15,17)	180.000
R(15,16)	1.088	A(2,15,16)	118.280	D(5,3,11,2)	179.999
R(15,17)	1.402	A(2,15,17)	123.837	D(14,6,7,10)	180.000
R(17,18)	1.223	A(8,19,18)	123.836	D(10,7,13,8)	180.000
R(18,19)	1.402	A 8,19,20)	118.280	D(19,8,13,7)	180.000
R(19,20)	1.088	A(18,19,20)	117.882	D(14,8,19,18)	180.000

Table 2.Optimized geometric parameters of compound 2

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,3)	1.346	A(3,1,8)	117.181	D(8,1,3,17)	179.997
R(1,8)	1.779	A(3,1,21)	127.716	D(21,1,3,7)	179.997
R(1,21)	1.503	A(8,1,21)	115.110	D(3,1,21,23)	120.367
R(2,8)	1.769	A(8,2,11)	123.640	D(8,1,21,24)	59.695
R(2,11)	1.361	A(5,4,29)	128.062	D(11,2,8,1)	179.996
R(21,22)	1.091	A(10,4,29)	115.281	D(8,2,11,12)	179.997
R(4,10)	1.778	A(10,6,15)	123.064	D(17,3,7,2)	179.998
R(4, 29)	1.503	A(1,8,2)	96.319	D(1,3,17,18)	120.292
R(6,15)	1.361	A(4,10,6)	96.548	D(7,3,17,19)	59.733
R(6,10)	1.771	A(2,11,12)	118.218	D(29,4,10,6)	179.992
R(11,12)	1.088	A(2,11,13)	123.937	D(5,4,29,31)	120.239
R(11,13)	1.403	A(12,11,13)	117.844	D(10,4,29,30)	179.962
R(13,14)	1.223	A(6,15,16)	118.218	D(10,4,29,32)	59.685
R(14,15)	1.403	A(1,21,23)	111.019	D(4,5,25,26)	120.317
R(29,30)	1.091	A(22,21,23)	107.884	D(9,5,25,28)	179.984

Table 3.Optimized geometric parameters of compound 3

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,3)	1.339	A(3,1,23)	113.195	D(23,1,3,7)	179.996
R(1,8)	1.759	A(8,1,23)	128.427	D(3,1,23,24)	120.324
R(1,23)	1.503	A(3,1,8)	118.376	D(8,1,23,25)	59.679
R(2,8)	1.785	A(7,2,8)	114.349	D(11,2,8,1)	179.999
R(4,10)	1.758	A(8,2,11)	123.108	D(17,3,7,2)	179.995
R(6,10)	1.785	A(5,4,10)	117.919	D(1,3,17,18)	120.245
R(6,15)	1.360	A(5,4,26)	113.463	D(7,3,17,19)	59.736
R(11,12)	1.088	A(10,4,26)	128.617	D(7,3,17,20)	179.993
R(11,13)	1.403	A(9,6,10)	114.349	D(10,4,5,29)	179.996
R(13,14)	1.223	A(4,10,6)	94.778	D(10,4,26,28)	59.736
R(2,11)	1.360	A(2,11,12)	118.241	D(3,17,20,21)	120.967
R(20,23)	1.564	A(2,11,13)	117.897	D(21,20,23,24)	118.892
R(23,25)	1.097	A(12,11,13)	117.861	D(27,26,32,34)	118.942
R(26,32)	1.565	A(6,15,16)	118.241	D(30,29,32,33)	118.892
R(32,34)	1.092	A(14,15,16)	117.861	D(31,29,32,26)	120.126

Table 4.Optimized geometric parameters of compound 4

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,3)	1.343	A(3,1,8)	117.496	D(8,1,3,17)	179.957
R(1,8)	1.773	A(3,1,20)	113.554	D(3,1,20,21)	106.519
R(2,11)	1.360	A(8,1,20)	118.617	D(8,1,20,22)	43.184
R(1,20)	1.508	A(8,2,11)	123.457	D(8,1,20,23)	165.307
R(2,8)	1.773	A(10,4,29)	118.830	D(7,2,11,13)	179.945
R(11,12)	1.088	A(1,8,2)	95.855	D(7,3,17,19)	43.087
R(6,10)	1.774	A(4,10,6)	96.050	D(7,3,17,26)	165.131
R(6,15)	1.360	A(2,11,12)	118.298	D(5,4,29,30)	106.379
R(11,13)	1.223	A(2,11,13)	123.837	D(32,5,9,6)	179.731
R(13,14)	1.223	A(6,15,14)	123.837	D(9,5,32,35)	165.307
R(15,16)	1.088	A(6,15,16)	118.298	D(5,32,35,38)	44.661
R(20,22)	1.096	A(1,20,22)	110.013	D(33,32,35,37)	162.602
R(20,23)	1.538	A(22,20,23)	110.131	D(32,35,38,39)	176.604
R(23,24)	1.095	A(20,23,24)	109.513	D(36,35,38,39)	54.681
R(23,26)	1.534	A(24,23,26)	110.483	D(37,35,38,29)	59.333

3.2. Molecular Electrostatic Potential (MEP)

The MEP is used for determining sites for electrophilic attack and nucleophilic reactions and correlates with many structural properties of molecule such as chemical reactivity and dipole moment ^[41]. Different colors are used for representation of different value of the electrostatic potential. Red color show electron rich area and blue color indicate electron deficient region of the molecule. Potential decreases in the order red < yellow < green < blue. As can be seen

from the Fig 2, these molecules have several possible sites for electrophilic and nucleophilic attacks.

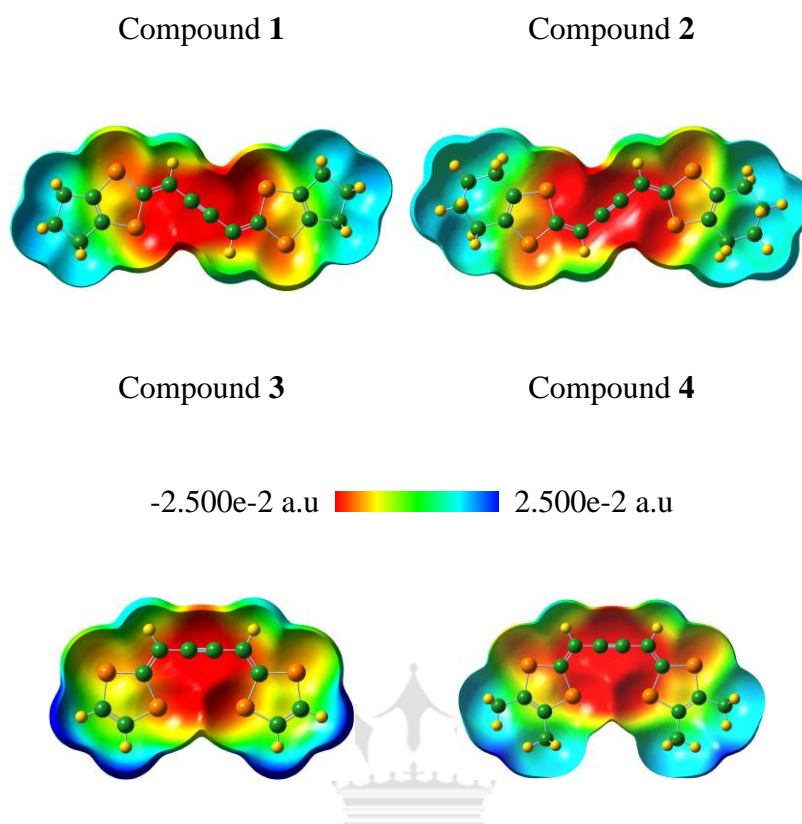


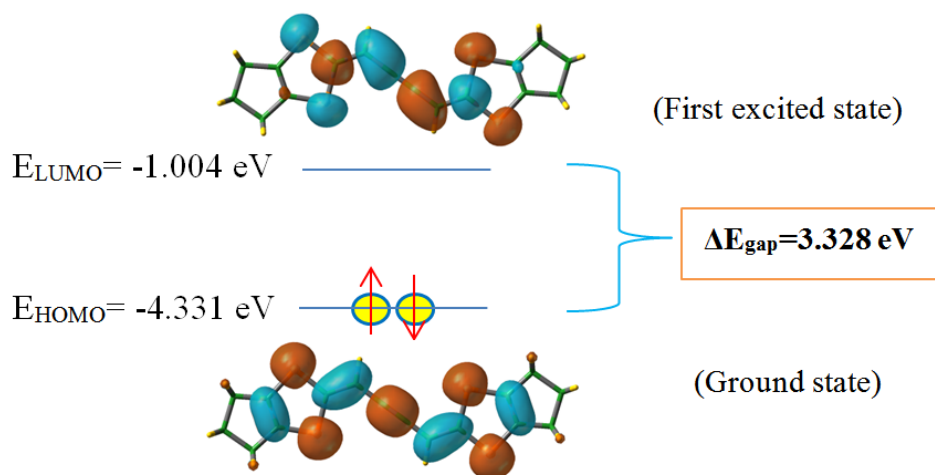
Figure 2. Molecular electrostatic potential surface of symmetrical acetylenic analogues of TTF 1-4

As seen from the figure that, in all molecules, the regions exhibiting the negative electrostatic potential are localized near the TTF core and the carbon chain that contains the alkyne function while the regions presenting the positive potential are localized vicinity of the hydrogen atoms of alkyl and cyclic groups.

3.3. Frontier Molecular Orbitals (FMOs)

HOMO-LUMO band gap plays a very crucial role in determining the chemical reactivity, stability of the molecule ^[42], chemical reactions, electrical properties and optical properties. LUMO energy means ability to accept an electron while HOMO energy means ability to donate an electron. Chemical reactivity of a molecule can be determined from the HOMO-LUMO band gap. A small band gap implies low kinetic stability of the molecule ^[43]. HOMO-LUMO separation is a result of significant degree of intermolecular charge transfer from

electron donor groups to the electro acceptor groups through π -conjugated paths. Energy gap between HOMO and LUMO has also been used to prove the bioactivity from intra-molecular charge transfer. The energy gap between HOMO and LUMO of compound **3** with a small gap and high reactivity is shown in Fig 3.



3.4. Global Reactivity Descriptors

The global chemical reactivity of molecules have been defined in terms of hardness (η), softness (S), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω) and local reactivity has been defined in terms of Fukui function and the philicity^[44-47]. Using Koopman's theorem for closed-shell molecules, η , S , μ , χ and ω are related as:

$$\eta = (I - A) / 2$$

$$\mu = -(I + A) / 2$$

$$\chi = (I + A) / 2 = -\mu$$

$$S = 1 / \eta$$

$$\omega = \mu^2 / 2\eta$$

$$I = -E_{\text{HOMO}} \text{ and } A = -E_{\text{LUMO}}$$

Where I and A are the ionization potential and electron affinity of the compounds. χ is the Mulliken electronegativity, because of the fundamental relationship to the chemical potential, therefore χ is a property of the entire molecule^[46]. In the reference global chemical reactivity

of molecules, the electrophilicity index (ω) is the most important descriptor. It is a measure of energy lowering due to maximal electron flow between donor and acceptor ^[45]. Thus global and local chemical reactivity descriptors of molecules are very useful parameters to define the intensity of chemical reactivity and site selectivity. Therefore by calculating these parameters, we can explain theoretically the chemically active properties of molecules. All the calculated values of ionization potential, electron affinity, hardness, potential, softness and electrophilicity index are shown in Table 5.

Table 5. Quantum chemical descriptors of symmetrical acetylenic analogues of TTF 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-4.511	-4.313	-4.331	-4.267
E_{LUMO} (eV)	-1.106	-0.913	-1.004	-0.911
ΔE_{gap} (eV)	3.405	3.400	3.328	3.356
I (eV)	4.551	4.313	4.331	4.267
A (eV)	1.106	0.913	1.004	0.911
μ (eV)	-2.808	-2.613	-2.667	-2.589
χ (eV)	2.808	2.613	2.667	2.589
η (eV)	1.703	1.700	1.664	1.678
S (eV)	0.294	0.294	0.300	0.298
ω (eV)	2.316	2.008	2.138	1.998

As presented in table 5, the compound which have the lowest energetic gap is the compound **3** ($\Delta E_{\text{gap}} = 3.328$ eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **1** ($\Delta E_{\text{gap}} = 3.405$ eV). The compound that has the highest HOMO energy is the compound **4** ($E_{\text{HOMO}} = -4.267$ eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **1** ($E_{\text{LUMO}} = -1.106$ eV) which signifies that it can be the best electron acceptor. The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound **4** has lowest value of the potential ionization ($I = 4.267$ eV), so that will be the better electron donor. Compound **1** has the largest value of the affinity ($A = 1.106$ eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness)

value of compound **3** ($\eta = 1.664$ eV, $S = 0.300$ eV) is lesser (greater) among all the molecules. Thus, compound **3** is found to be more reactive than all the compounds. Compound **1** possesses higher electronegativity value ($\chi = 2.808$ eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **1** ($\omega = 2.316$ eV) indicates that it is the stronger electrophiles than all compounds. Compound **3** has the smaller frontier orbital gap so, it is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

3.5. Local Reactivity Descriptors

The Fukui function has been widely used as a single-reactant chemical reactivity descriptor [48]. In general, for a system with n electrons, the two Fukui functions proposed by Yang [49] are:

$$f_k^- = q_k(n) - q_k(n-1)$$

$$f_k^+ = q_k(n+1) - q_k(n)$$

Where $q_k(n)$, $q_k(n+1)$ and $q_k(n-1)$ represent the electronic population of atom k in the system with n , $n+1$ and $n-1$ electrons, respectively. The two Fukui function indices provide a successful way of measuring the reactivity of regions of clusters [50-52]. The local site with high f_k^- value will easily react with electron acceptors, whereas the local site where f_k^+ is large will well react with electron donors. Fukui functions for selected atomic sites in symmetrical acetylenic analogues of TTF **1-4** are shown in Tables 6-7.

Table 6. Order of the reactive sites on compounds 1 and 2

Compound 1					Compound 2				
Atom	18 C	17 C	1 C	7 C	Atom	1 C	5 C	4 C	3 C
f^+	0.004	0.004	-0.035	-0.035	f^+	0.018	0.018	0.014	0.014
Atom	8 C	2C	3 C	6 C	Atom	3 C	4 C	2 C	6 C
f^-	0.007	0.007	-0.055	-0.055	f^-	0.007	0.007	0.005	0.005
Atom	8 C	2 C	18 C	17 C	Atom	4 C	3 C	1 C	5 C
f^0	-0.016	-0.016	-0.031	-0.031	f^0	0.010	0.010	0.008	0.008

Table 7. Order of the reactive sites on compounds 3 and 4

Compound 3					Compound 4				
Atom	4 C	3 C	1 C	5 C	Atom	3 C	4 C	1 C	5 C
f^+	0.019	0.019	0.017	0.017	f^+	0.014	0.014	0.014	0.014
Atom	2C	6 C	4 C	3 C	Atom	2 C	6 C	3 C	4 C
f^-	0.009	0.009	0.005	0.005	f^-	0.007	0.007	0.004	0.004
Atom	4 C	3 C	1 C	5 C	Atom	3 C	4 C	1 C	5 C
f^0	0.012	0.012	0.010	0.010	f^0	0.009	0.009	0.008	0.008

From the tables 6-7, the parameters of local reactivity descriptors show that 18C, 1C, 4C and 3C are the more reactive sites in compounds **1**, **2**, **3** and **4** respectively for nucleophilic attacks. The more reactive sites in radical attacks are 8C, 3C, for compounds **1**, **4** and 4C for compounds **2** and **3** respectively. The more reactive sites for electrophilic attacks are 8C, 3C for compounds **1**, **2** and 2C for compounds **3** and **4** respectively.

3.6. Natural Bond Orbital Analysis (NBO)

The NBO calculations were performed using the DFT/B3LYP/6-31G(d,p) level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the inter-molecular delocalization or hyperconjugation. It is an essential tool for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory is reported ^[53,54]. The second-order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis. The output obtained by the 2nd order perturbation theory analysis is normally the first to be examined by the experienced NBO user in searching for significant delocalization effects. However, the strengths of these delocalization interactions, $E(2)$, are estimated by second order perturbation theory ^[55] as estimated by Eq.

$$E_2 = \Delta E_{ij} = q_i \frac{F^2(i, j)}{\epsilon_j - \epsilon_i}$$

q_i is the donor orbital occupancy; ϵ_i , ϵ_j is the diagonal elements and F_{ij} is the off diagonal NBO Fock matrix element. The energy values for the interaction between the filled (donors) i and vacant (acceptors) orbital j , calculated by the second order perturbation theory have been tabulated Tables 8-11. The larger the $E(2)$ value, the more intensive is the interaction between

electron donors and acceptors, i.e. the more the electrons donating tendency from electron donors to acceptors.

Table 8. Second order perturbation theory analysis of Fock matrix on NBO of compound 1

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP(2)S12	1.74344	$\pi^*(C1-C3)$	0.21999	22.73	0.25	0.068
LP(2)S13	1.74345	$\pi^*(C6-C7)$	0.21999	22.73	0.25	0.068
LP(2)S11	1.75050	$\pi^*(C1-C3)$	0.21999	22.23	0.25	0.068
LP(2)S14	1.75050	$\pi^*(C6-C7)$	0.21999	22.23	0.25	0.068
LP(2)S12	1.74344	$\pi^*(C2-C15)$	0.34889	21.06	0.26	0.068
LP(2)S13	1.74345	$\pi^*(C8-C19)$	0.34889	21.06	0.26	0.068
LP(2)S11	1.75050	$\pi^*(C2-C15)$	0.34889	19.20	0.27	0.066
LP(2)S14	1.75050	$\pi^*(C8-C19)$	0.34889	19.20	0.27	0.066
$\sigma(C15-C17)$	1.97285	$\sigma^*(C17-C18)$	0.02349	12.24	1.68	0.128
$\sigma(C18-C19)$	1.97285	$\sigma^*(C17-C18)$	0.02349	12.24	1.68	0.128
$\sigma(C17-C18)$	1.97864	$\sigma^*(C15-C17)$	0.02000	9.45	1.41	0.103
$\sigma(C17-C18)$	1.97864	$\sigma^*(C18-C19)$	0.02000	9.45	1.41	0.103
$\sigma(C15-H16)$	1.95835	$\sigma^*(C2-S12)$	0.04370	7.40	0.69	0.064
$\sigma(C19-H20)$	1.95835	$\sigma^*(C8-S13)$	0.04370	7.40	0.69	0.064
$\sigma(C1-H4)$	1.97598	$\sigma^*(C3-S11)$	0.01740	5.34	0.76	0.057
$\sigma(C7-H10)$	1.97598	$\sigma^*(C6-S14)$	0.01740	5.34	0.76	0.057
$\sigma(C3-H5)$	1.97642	$\sigma^*(C1-S12)$	0.01929	5.25	0.77	0.057
$\sigma(C6-H9)$	1.97642	$\sigma^*(C7-S13)$	0.01740	5.25	0.77	0.057
$\sigma(C15-C17)$	1.97285	$\sigma^*(C18-C19)$	0.02000	4.63	1.29	0.069
$\sigma(C18-C19)$	1.97285	$\sigma^*(C15-C17)$	0.02000	4.63	1.29	0.069

Table 9.Second order perturbation theory analysis of Fock matrix on NBO of compound 2

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP(2)S8	1.75748	$\pi^*(C2-C11)$	0.34832	21.63	0.26	0.069
LP(2)S9	1.75748	$\pi^*(C6-C15)$	0.34832	21.63	0.26	0.069
LP(2)S8	1.75748	$\pi^*(C1-C3)$	0.23803	20.87	0.27	0.067
LP(2)S9	1.75748	$\pi^*(C4-C5)$	0.23803	20.87	0.27	0.067
LP(2)S7	1.76549	$\pi^*(C1-C3)$	0.23803	20.33	0.27	0.066
LP(2)S10	1.76549	$\pi^*(C4-C5)$	0.23803	20.33	0.27	0.066
LP(2)S7	1.76549	$\pi^*(C2-C11)$	0.34832	19.61	0.27	0.066
LP(2)S10	1.76549	$\pi^*(C6-C15)$	0.34832	19.61	0.27	0.066
$\sigma(C11-C13)$	1.95875	$\sigma^*(C13-C14)$	0.02349	12.24	1.68	0.128
$\sigma(C14-C15)$	1.97304	$\sigma^*(C13-C14)$	0.02349	12.24	1.68	0.128
$\sigma(C13-C14)$	1.97865	$\sigma^*(C11-C13)$	0.02006	9.44	1.41	0.103
$\sigma(C13-C14)$	1.97865	$\sigma^*(C14-C15)$	0.02006	9.44	1.41	0.103
$\sigma(C11-H12)$	1.95875	$\sigma^*(C2-S8)$	0.04049	7.40	0.70	0.064
$\sigma(C15-H16)$	1.95875	$\sigma^*(C6-S9)$	0.04049	7.40	0.70	0.064
$\sigma(C1-S8)$	1.97245	$\sigma^*(C3-C17)$	0.01872	5.23	1.04	0.066
$\sigma(C5-S9)$	1.97245	$\sigma^*(C4-C29)$	0.01872	5.23	1.04	0.066
$\sigma(C3-S7)$	1.97315	$\sigma^*(C1-C21)$	0.01854	5.19	1.04	0.066
$\sigma(C4-S10)$	1.97315	$\sigma^*(C5-C25)$	0.01854	5.19	1.04	0.066
$\sigma(C3-C17)$	1.97938	$\sigma^*(C1-C3)$	0.02993	5.15	1.29	0.073
$\sigma(C4-C29)$	1.97938	$\sigma^*(C4-C5)$	0.02993	5.15	1.29	0.073

Table 10.Second order perturbation theory analysis of Fock matrix on NBO of compound 3

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP(2)S8	1.75506	$\pi^*(C1-C3)$	0.24547	22.63	0.27	0.070
LP(2)S9	1.75506	$\pi^*(C4-C5)$	0.24547	22.63	0.27	0.070
LP(2)S7	1.76117	$\pi^*(C1-C3)$	0.24547	22.01	0.27	0.069
LP(2)S10	1.76117	$\pi^*(C4-C5)$	0.24547	22.01	0.27	0.069
LP(2)S8	1.75506	$\pi^*(C2-C11)$	0.33996	20.55	0.26	0.067
LP(2)S9	1.75506	$\pi^*(C6-C15)$	0.33996	20.55	0.26	0.067
LP(2)S7	1.76117	$\pi^*(C2-C11)$	0.33996	18.71	0.27	0.065
LP(2)S10	1.76117	$\pi^*(C6-C15)$	0.33996	18.71	0.27	0.065
$\sigma(C11-C13)$	1.97268	$\sigma^*(C13-C14)$	0.02357	12.24	1.68	0.128
$\sigma(C14-C15)$	1.97268	$\sigma^*(C13-C14)$	0.02357	12.24	1.68	0.128
$\sigma(C13-C14)$	1.97864	$\sigma^*(C11-C13)$	0.02009	9.45	1.41	0.103
$\sigma(C13-C14)$	1.97864	$\sigma^*(C14-C15)$	0.02009	9.45	1.41	0.103
$\sigma(C11-H12)$	1.95790	$\sigma^*(C2-S8)$	0.04211	7.40	0.69	0.064
$\sigma(C15-H16)$	1.95790	$\sigma^*(C6-S9)$	0.04211	7.40	0.69	0.064
$\sigma(C17-C20)$	1.97955	$\sigma^*(C3-S7)$	0.02791	6.13	0.78	0.062
$\sigma(C26-C32)$	1.97955	$\sigma^*(C4-S10)$	0.02791	6.13	0.78	0.062
$\sigma(C20-C23)$	1.97986	$\sigma^*(C1-S8)$	0.02925	5.98	0.79	0.061
$\sigma(C29-C32)$	1.97986	$\sigma^*(C5-S9)$	0.02925	5.98	0.79	0.061
$\sigma(C1-C23)$	1.97498	$\sigma^*(C3-S7)$	0.02791	5.51	0.84	0.061
$\sigma(C5-C29)$	1.97498	$\sigma^*(C4-S10)$	0.02791	5.51	0.84	0.061

Table 11.Second order perturbation theory analysis of Fock matrix on NBO of compound 4

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP(2)S8	1.99864	$\pi^*(\text{C1-C3})$	0.24067	21.32	0.27	0.068
LP(2)S9	1.99864	$\pi^*(\text{C4-C5})$	0.24067	21.32	0.27	0.068
LP(2)S8	1.99864	$\pi^*(\text{C2-C11})$	0.34511	21.29	0.26	0.069
LP(2)S9	1.99864	$\pi^*(\text{C6-C15})$	0.34511	21.29	0.26	0.069
LP(2)S7	1.76354	$\pi^*(\text{C1-C3})$	0.24067	20.75	0.27	0.067
LP(2)S10	1.76354	$\pi^*(\text{C4-C5})$	0.24067	20.75	0.27	0.067
LP(2)S7	1.76354	$\pi^*(\text{C2-C11})$	0.34511	19.42	0.27	0.066
LP(2)S10	1.76354	$\pi^*(\text{C6-C15})$	0.34511	19.42	0.27	0.066
$\sigma(\text{C11-C13})$	1.97294	$\sigma^*(\text{C13-C14})$	0.02360	12.24	1.68	0.128
$\sigma(\text{C14-C15})$	1.97294	$\sigma^*(\text{C13-C14})$	0.02360	12.24	1.68	0.128
$\sigma(\text{C13-C14})$	1.97865	$\sigma^*(\text{C11-C13})$	0.02008	9.44	1.41	0.103
$\sigma(\text{C13-C14})$	1.97865	$\sigma^*(\text{C14-C15})$	0.02008	9.44	1.41	0.103
$\sigma(\text{C11-H12})$	1.95867	$\sigma^*(\text{C2-S8})$	0.04102	7.40	0.69	0.064
$\sigma(\text{C15-H16})$	1.95867	$\sigma^*(\text{C6-S9})$	0.04102	7.40	0.69	0.064
$\sigma(\text{C3-C17})$	1.97331	$\sigma^*(\text{C1-C3})$	0.02966	5.06	1.28	0.072
$\sigma(\text{C4-C29})$	1.97331	$\sigma^*(\text{C4-C5})$	0.02966	5.06	1.28	0.072
$\sigma(\text{C1-C20})$	1.97331	$\sigma^*(\text{C1-C3})$	0.02966	5.02	1.28	0.072
$\sigma(\text{C5-C32})$	1.97331	$\sigma^*(\text{C4-C5})$	0.02966	5.02	1.28	0.072
$\sigma(\text{C11-C13})$	1.97294	$\sigma^*(\text{C14-C15})$	0.02008	4.63	1.29	0.069
$\sigma(\text{C14-C15})$	1.97294	$\sigma^*(\text{C11-C13})$	0.02008	4.63	1.29	0.069

The intramolecular interaction for the title compounds is formed by the orbital overlap between: $\sigma(\text{C15-C17})$ and $\sigma^*(\text{C17-C18})$ for compound **1**, $\sigma(\text{C11-C13})$ and $\sigma^*(\text{C13-C14})$ for compound **2**, $\sigma(\text{C11-C13})$ and $\sigma^*(\text{C13-C14})$ for compound **3** and $\sigma(\text{C11-C13})$ and $\sigma^*(\text{C13-C14})$ for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intramolecular hyper conjugative interactions of

$\sigma(\text{C15-C17})$ to $\sigma^*(\text{C17-C18})$ for compound **1**, $\sigma(\text{C11-C13})$ to $\sigma^*(\text{C13-C14})$ for compound **2**, $\sigma(\text{C11-C13})$ to $\sigma^*(\text{C13-C14})$ for compound **3** and $\sigma(\text{C11-C13})$ to $\sigma^*(\text{C13-C14})$ for compound **4** lead to highest stabilization of 12.24, 12.24, 12.24 and 12.24 kJ mol⁻¹ respectively. In case of LP(2)S12 orbital to the $\pi^*(\text{C1-C3})$ for compound **1**, LP(2)S8 orbital to $\pi^*(\text{C2-C11})$ for compound **2**, LP(2)S8 orbital to $\pi^*(\text{C1-C3})$ for compound **3**, LP(2)S8 orbital to $\pi^*(\text{C1-C3})$ for compound **4** respectively, show the stabilization energy of 22.73, 22.63, 22.63 and 21.32 kJ mol⁻¹ respectively.

3.7. Nonlinear Optical Properties (NLO)

The NLO activity provide the key functions for frequency shifting, optical modulation, optical switching and optical logic for the developing technologies in areas such as communication, signal processing and optical interconnections [56,57]. The first static hyperpolarizability (β_o) and its related properties (β , α_o and $\Delta\alpha$) have been calculated using DFT/B3LYP/6-31G(d,p) level based on finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field and the first hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components because of the Kleinman symmetry [58]. The matrix can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrices is a tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field.

When the external electric field is weak and homogeneous, this expansion is given below:

$$E = E^0 - \mu_i F_i - 1/2 \alpha_{ij} F_i F_j - 1/6 \beta_{ijk} F_i F_j F_k + \dots$$

Where E^0 is the energy of the unperturbed molecules, F_α is the field at the origin, μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and first hyperpolarizability, respectively. The total static dipole moment μ , the mean polarizability α_o , the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability β_o , using the x, y and z components are defined as:

Dipole moment is

$$\mu_{\text{tot}} = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2}$$

Static polarizability is

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

Total polarizability is

$$\Delta\alpha = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2]^{1/2}$$

First order hyperpolarizability is

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Where

$$\beta_x = \beta_{xxx} + \beta_{xyz} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The total molecular dipole moment (μ), mean polarizability (α_0) and anisotropy polarizability ($\Delta\alpha$) and first hyperpolarizability (β_{total}) of symmetrical acetylenic analogues of TTF **1-4** are computed and are depicted in Table 12.

Table 12. The dipole moments μ (D), polarizability α , the average polarizability α (esu), the anisotropy of the polarizability $\Delta\alpha$ (esu), and the first hyperpolarizability β (esu) of symmetrical acetylenic analogues of TTF 1-4 calculated by B3LYP/6-31G(d,p) method

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	0.0013	0.0149	-0.0017	0.0011
B_{yyy}	-24.6130	23.2484	0.0001	0.0000
B_{zzz}	0.0001	0.0004	0.0048	0.8848
B_{xyy}	-0.0004	-0.0017	0.0002	0.0000
B_{xxy}	-67.4078	83.1360	0.0014	0.0006
B_{xxz}	0.0020	0.0056	0.0233	3.7063
B_{xzz}	0.0000	0.0005	0.0000	0.0000
B_{yzz}	-1.7130	9.1643	0.0002	0.0001
B_{yyz}	0.0006	-0.0011	-0.0008	0.5270
B_{xyz}	-0.0086	0.0171	0.0031	-1.1139
$B_{tot}(\text{esu}) \times 10^{-33}$	93.7338	115.5487	83.0274	75.2377
μ_x	0.0000	0.0003	0.0000	0.0000
μ_y	-2.8187	4.1517	0.0001	0.0000
μ_z	0.001	0.0001	0.0006	0.1000
$\mu_{tot}(\text{D})$	2.8187	4.1517	3.0006	2.1000
α_{xx}	-83.8045	-101.8132	-87.8656	-94.8371
α_{yy}	-95.4582	-122.4187	-139.1124	-151.6173
α_{zz}	-115.0050	-139.7871	-148.6449	-162.1576
α_{xy}	0.0000	-0.0005	7.8704	-7.3703
α_{xz}	0.0040	0.0053	-0.0007	-0.0001
α_{yz}	-0.0005	-0.0002	-0.0001	-0.0001
$\alpha(\text{esu}) \times 10^{-24}$	27.3071	32.9262	58.2361	64.0042
$\Delta\alpha(\text{esu}) \times 10^{-24}$	4.0469	4.8797	8.6306	9.4854

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_{tot}) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been

converted into electrostatic units (e.s.u.) (for α ; 1 a.u. = 0.1482×10^{-24} e.s.u., for β ; 1 a.u. = 8.6393×10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 2.8187, 4.1517, 3.0006 and 2.1000 D respectively, which are approximately four times than to the value for urea ($\mu = 1.3732$ D). Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it has been used frequently as a threshold value for comparative purposes. The calculated values of polarizability are 27.3071×10^{-24} , 32.9262×10^{-24} , 58.2361×10^{-24} and 64.0042×10^{-24} esu respectively; the values of anisotropy of the polarizability are 4.0469, 4.8797, 8.6306 and 9.4854 esu, respectively. The magnitude of the molecular hyperpolarizability (β) is one of important key factors in a NLO system. The DFT/6-31G(d,p) calculated first hyperpolarizability value (β) of symmetrical acetylenic analogues of TTF molecules are equal to 93.7338×10^{-33} , 115.5487×10^{-33} , 83.0274×10^{-33} and 75.2377×10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.27, 0.34, 0.24 and 0.22 times than those of urea (β of urea is 343.272×10^{-33} esu obtained by B3LYP/6-311G (d,p) method). This result indicates that symmetrical acetylenic analogues of TTF **1-4** are not nonlinear.

4. CONCLUSION

In this work, the computations were performed at B3LYP/6-31G basis to get the optimized geometry of the symmetrical acetylenic analogues of TTF **1-4**. The HOMO and LUMO analysis is used to determine the charge transfer within the molecules. The stability of the molecules arising from hyper-conjugative interaction and charge delocalization has been analyzed using NBO analysis. From the MEP it is evident that the negative charge covers the TTF core and the carbon chain that contains the alkyne function and the positive region is over the hydrogen atoms of alkyl and cycled groups.

The predicted NLO properties of the title compounds are much smaller than those of urea, which indicating that it is not suitable for the manufacture of organic materials.

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